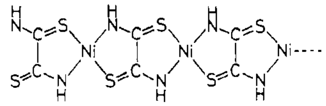

Figure 3. Proposed structure of the Ni–RA complex in the interlayer region of MoO_3.

sulfur atoms of rubeanic acid molecule. Coordinate bond and coordination forces cause the frequencies of these groups to undergo a considerable displacement.

From the measurement of the magnetic susceptibility, the RA–Ni–MoO_3 complex was found to be nearly diamagnetic, while $Ni_{0.25}(H_2O)_nMoO_3$ showed paramagnetic behavior. This result indicates that the rubeanic acids are linking to Ni(II) ions so as to form a square-planar configuration. In contrast, the Ni–RA complex, prepared by the usual precipitate method, exhibited paramagnetic behavior. From this magnetic property, it was concluded that the Ni–RA complex consists of both coplanar and octahedral configurations about the nickel atoms.[12,13]

The electrical resistivities of $Na_{0.5}(H_2O)_nMoO_3$ and $Ni_{0.25}(H_2O)_nMoO_3$ were found to be about 20–30 Ω cm at room temperature; however, in the case of RA–Ni–MoO_3, the electrical resistivity was about 10^6 Ω cm. This high electrical resistivity could be explained by localization of negative charges on MoO_3 layers, which was caused by bond formation between O atoms of MoO_3 layers and H^+ ions released from N atoms of rubeanic acid by chelation with Ni^{2+} ions. The agreement of H values of RA–Ni–MoO_3 between the calculated and found values also indicated the presence of H^+ ions in the interlayer region of MoO_3 layers. Further, the existence of O–H bonding was recognized by the fact that a broad band around 3380 cm^{-1} assignable to stretching vibration of OH was found in the IR spectrum of RA–Ni–MoO_3. From these results, it might be considered that the neutral Ni–RA complex was formed in the interlayer space of MoO_3.

The present results are summarized below. In this study Ni(II)–RA coordination polymer was first prepared in the interlayer region of MoO_3. The molecular structure was estimated from the results of X-ray, DTA, TG, IR, and chemical analyses of the complex and the magnetic susceptibility. These results suggest a possible structure of the intercalated Ni–RA complex as follows: each Ni(II) ion is coordinated with rubeanic acid molecules maintaining the molar ratio of rubeanic acid and Ni(II) ion to be 1:1, and as a whole the Ni–RA complex forms a linear polymeric configuration as illustrated in Figure 3.

This structure could be supported by the following considerations. The interatomic distance between Ni^{2+} ions of the above mentioned model is in good agreement with that obtained from an approximate calculation, assuming even distribution of Ni^{2+} ions in $Ni_{0.25}MoO_3$. Further, rubeanic acid takes a trans conformation in the solid state,[14] and this chelating ligand has a tendency to coordinate with Ni^{2+} ion to give a chelate complex. In the future the authors will attempt to remove the intercalated Ni–RA complex from MoO_3.

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Registry No. MoO_3, 1313-27-5; $Na_{0.5}(H_2O)_nMoO_3$, 68510-66-7; $Ni_{0.25}(H_2O)_nMoO_3$, 68510-67-8; Ni–RA, 54787-47-2; RA, 79-40-3.

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On the Role of the Bridging Ligand in Electrochemical Inner-Sphere Electron-Transfer Processes

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The treatment of the relative electron-transfer rates for electrochemical inner- and outer-sphere pathways in terms of "intrinsic" and "thermodynamic" contributions is discussed in order to explore the possible roles of bridging ligands in catalyzing such processes. By combining rate measurements with adsorption data for the appropriate ligand-bridged intermediates, this treatment has been applied to some inner- and outer-sphere reactions involving Cr(III)/Cr(II) and Co(III)/Co(II) couples at the mercury–aqueous interface. For complexes containing azide and thiocyanate bridging ligands, the rate increases that result from the presence of ligand-bridged pathways appear to arise merely from the presence of more favorable thermodynamic work terms, rather than by a decrease in the reorganization energy required for electron transfer. A similar conclusion applies, although with less certainty, to chloride and bromide bridges. The physical relation between the reorganization barriers for heterogeneous and homogeneous inner-sphere processes is also considered, and the extent of catalysis of heterogeneous and homogeneous Cr(III)/Cr(II) exchange reactions by bridging anions is compared. Sizable decreases in the intrinsic reorganization barrier for ligand-bridged vs. outer-sphere pathways are seen for the homogeneous exchange reactions, but negligible or only modest decreases are seen for the corresponding electrochemical processes. The explanation for these differences is sought in terms of electronic coupling effects between the homogeneous reacting centers.

Introduction

The structure of the electrode–solution interface is both expected and generally found to have a marked influence on the kinetics of heterogeneous electron-transfer reactions. This influence is simplest and best understood for electrode reactions that proceed via outer-sphere pathways, i.e., where both the reactant's and the electrode's coordinated ligands remain intact during electron transfer,[1] since only weak electrostatic interactions are anticipated between the reactant and the electrode surface. Indeed, the close relationship between the rates of adiabatic outer-sphere redox reactions in homogeneous solution and at inert metal electrodes that is predicted by the Marcus[2] and other contemporary theories of electron transfer[3] is for the most part borne out by the available experimental data.[2b,4,5]

However, for many homogeneous redox reactions, inner-sphere mechanisms where the two reacting centers share a common ligand provide the dominant reaction pathway.[6] Inner-sphere pathways are also expected to be followed by many electrochemical inorganic redox reactions where the solvent layer immediately adjacent to the electrode surface is displaced by the reactant or a ligand coordinated to the reactant prior to electron transfer.[1] Indeed, the marked catalyses induced by adsorbing ligands that are observed for many electrode processes involving cationic reactants can often be attributed to the occurrence of inner-sphere pathways.[7] However, many of these reactions involve multielectron transfer and transition states of ill-defined structure. Recently, methods for distinguishing between some simple electrochemical inner- and outer-sphere mechanisms have been developed and applied to the one-electron electroreduction of various aquo[8] and ammine complexes[1] of Cr(III), as well as Eu(III)[9] and pentaamminecobalt(III)[10] at the mercury–aqueous interface. These electrode reactions involving Cr(III) and Co(III) complexes are of particular interest because they are the direct heterogeneous analogues of the classical homogeneous redox reactions for which both inner- and outer-sphere transition pathways can be clearly identified.[6] Since these reactants are inert to ligand substitution, the composition of the coordination sphere can be controlled independently of the solution composition. For a number of these complexes that contain adsorbing anionic ligands, inner-sphere mechanisms involving anion bridging clearly provide the dominant electroreduction pathways.[8-10] However, for the majority of these reactants and particularly for pentaamminechromium(III) and -cobalt(III), only modest differences in reduction rate are observed for inner-sphere as compared with closely similar reactions that proceed via outer-sphere pathways, and mixed mechanisms are encountered for some systems even when the free bridging anions are known to be specifically adsorbed.[1,10] In contrast, much larger rate differences have commonly been observed between otherwise similar homogeneous inner- and outer-sphere reactions involving Cr(III)/Cr(II) and Co(III)/Co(II) redox couples.[6,11]

Reactivity patterns are more difficult to analyze for inner- compared to outer-sphere reactions due to the strong mutual interactions experienced by the reacting centers in the former mechanism. Nevertheless, the study of inner-sphere reactivity patterns has been actively pursued for a large variety of homogeneous redox reactions, especially with a view to unraveling the roles of the bridging ligand in catalyzing such processes between metal ions.[11] For this purpose, it has been found useful to factorize the variations in the observed rate constant into various distinct contributions arising from variations in the stabilities of the precursor and successor complexes, the standard free energy change for the overall reaction, and the reorganization energy required for electron transfer within the binuclear intermediate.[11-13] Little direct information is available regarding the absolute values of these terms for most homogeneous reactions. However, qualitative or semiquantitative relative estimates can be made for some systems which have led to interesting and stimulating insights into the role of the bridging ligand in homogeneous redox processes.[11-13]

Similar difficulties hamper the quantitative treatment of electrochemical inner-sphere reactivity patterns. Indeed, few previous attempts seem to have been made to unravel these factors for electrochemical reactions, despite their fundamental importance. One reason may be the paucity of experimental information on the adsorption thermodynamics of the reaction intermediates. However, the thermodynamic stabilities of the precursor complexes (i.e., the specifically adsorbed intermediates) for some inner-sphere reductions of Cr(III) complexes at mercury electrodes can be estimated with chronocoulometry[14] and from the influence of these adsorbates upon the outer-sphere reduction rates of cobalt(III)–ammine complexes.[15] The analysis of these and other pieces of experimental information, combined with the inner-sphere reduction rates themselves, allow the underlying roles of bridging ligands in these simple electrochemical reactions to be explored and compared with those for the corresponding homogeneous inner-sphere processes. Such an analysis forms the objective of the present communication.

Rate Formulations

A formalism similar to that originally due to Marcus[2] which is particularly useful for separating the disparate structural influences upon the rates of adiabatic redox reactions is expressed for electrochemical and chemical reactions in eq 1 and 2, respectively. k_e^E is the heterogeneous rate constant (cm s^{-1})

$$\ln k_e^E = \ln K_e^p + \ln \nu_e^p - \frac{1}{RT}(\Delta G_e^{\ddagger-p})^E \qquad (1a)$$

$$(\Delta G_e^{\ddagger-p})^E = (\Delta G_e^{\ddagger})^i - 0.5RT(\ln K_e^s - \ln K_e^p) + 0.5F(E - E^\circ) \qquad (1b)$$

$$\ln k_c = \ln K_c^p + \ln \nu_c^p - \frac{1}{RT}(\Delta G_c^{\ddagger-p}) \qquad (2a)$$

$$\Delta G_c^{\ddagger-p} = (\Delta G_c^{\ddagger})^i - 0.5RT(\ln K_c^s - \ln K_c^p) + 0.5\Delta G_c \qquad (2b)$$

for a one-electron electrochemical reduction measured at an electrode potential E, E° is the standard potential of the redox couple, k_c is the rate constant (M^{-1} s^{-1}), and ΔG_c° is the overall standard free energy change for the homogeneous reaction. K^p and K^s are the equilibrium constants for the formation of the binuclear "precursor" and "successor" ground states[12,13] from the separated reactants and products, ν^p is a frequency factor for activation within the binuclear intermediate,[13] $\Delta G^{\ddagger-p}$ is the standard free energy difference between the precursor and activated states, and $(\Delta G^{\ddagger})^i$ is the "intrinsic" free energy of reorganization[2,12] ("intrinsic barrier").

Equations 1a,b and 2a,b have a slightly different form to those of Marcus.[2] Firstly, the quadratic driving force terms[2] have been omitted. For small or moderate driving forces (i.e., $F(E - E^\circ)$ or ΔG_c°) these quadratic terms are negligible, and in any case their presence leads to poorer fits to experimental rate–potential plots for the outer-sphere electroreduction of some Cr(III) complexes.[16] Secondly, eq 1a and 2a contain a unimolecular frequency factor ν^p (s^{-1}) in place of the collision frequencies employed in the Marcus approach;[2] the "work terms" are written as equilibrium constants K^p and K^s. This formalism is preferred here because it is appropriate to inner- as well as outer-sphere processes, where well-defined binuclear intermediates are formed prior to the activation process.[13] Indeed approximate values of K_e^p can be obtained for a number of ligand-bridged reactions (see below). Although such relations were originally derived from the Marcus theory of outer-sphere processes, they have a purely phenomenological basis and should apply irrespective of the mechanism or the details of the activation process,[3] providing that the barrier to electron transfer is symmetrical[17] and the reactions are adiabatic.[20,21]

The first and the last two terms on the right-hand side of eq 1b and 2b can be considered to represent "intrinsic" and "thermodynamic" contributions, respectively, to the free energy of activation $\Delta G^{\ddagger-p}$.[22,23] Essentially, these "thermodynamic" terms describe how $\Delta G^{\ddagger\text{-p}}$ is modified as a result of variations in the free energies of the precursor and successor states. When these states are of equal energy, then $\Delta G^{\ddagger\text{-p}} = (\Delta G^{\ddagger})^{\text{i}}$. In addition, the ln K^{p} term in eq 1a,b can be considered to be a thermodynamic contribution to the observed rate constants, which takes into account the varying concentration of the precursor intermediate with respect to the bulk reactant.

In order to understand the role of coordinated ligands in electron-transfer kinetics and in particular that of bridging ligands in inner-sphere reactions, it is desirable to extract estimates of the intrinsic free energy of reorganization $(\Delta G^{\ddagger})^{\text{i}}$ from experimental rate and equilibrium data.[2,12] Variations in $(\Delta G^{\ddagger})^{\text{i}}$ that may occur as the physical and chemical state of the system is varied, i.e., by altering the coordinated ligands or reaction mechanism, reflect changes in the free energy of the activated state that are not accompanied by variations in the mean free energies of the adjacent precursor and successor ground states. $(\Delta G^{\ddagger})^{\text{i}}$ therefore provides a measure of the "special" properties of the activated state that are absent from the two ground states (precursor and successor states) that are adjacent to it in the reaction coordinate profile. For outer-sphere reactions, changes in rate which occur as the coordinated ligands are varied will chiefly reflect changes in $(\Delta G^{\ddagger})^{\text{i}}$ and the thermodynamic driving force term $[F(E - E^{\circ})$ or $\Delta G^{\circ}]$ since the work terms $RT \ln K^{\text{p}}$ and $RT \ln K^{\text{s}}$ are determined by nonspecific electrostatic and statistical factors. Variations in $(\Delta G^{\ddagger})^{\text{i}}$ can arise from changes in the force constants of bonds and the extent of solvent reorganization.[2,3] For inner-sphere reactions, the work terms $RT \ln K^{\text{p}}$ and $RT \ln K^{\text{s}}$ arise from short-range interactions and therefore can have a large and specific effect upon the observed rates. The nature of the coordinated ligands can affect $(\Delta G^{\ddagger})^{\text{i}}$ in the same way as for outer-sphere reactions. However, an important additional role of the bridging ligand may be to lower $(\Delta G^{\ddagger})^{\text{i}}$ by increasing the extent of "resonance splitting" at the intersection of the reactant's and product's potential energy surfaces.[12,13] The analysis of some suitable systems will now be undertaken in terms of eq 1 and 2 with the aim of deriving at least relative estimates of $(\Delta G^{\ddagger})^{\text{i}}$ for inner- vs. outer-sphere processes.

Estimation of Relative Electrochemical Intrinsic Barriers

Azide and Thiocyanate Bridges. Of the simple inorganic bridges that have been commonly found to mediate electrochemical electron-transfer reactions, azide and thiocyanate provide systems of particular interest. Thus both NCS^- and N_3^- exhibit similar complexing properties toward transition-metal cations yet are adsorbed to markedly different extents at mercury electrodes. In particular, the binding between these polyatomic ligands and the metal surface is unlikely to be affected greatly by the presence of the metal cation–ligand bonds, so that the values of K_{e}^{p} and K_{e}^{s} for the adsorbed intermediates are expected to be similar to those for the free anions, thus facilitating the estimation of $(\Delta G^{\ddagger})^{\text{i}}$.

Although K_{e}^{p} and K_{e}^{s} cannot be predicted theoretically to a useful precision, these quantities can be measured for some systems by detecting the adsorbed intermediates in potential regions where they are stable with respect to reduction or oxidation. The most suitable detection technique is chronocoulometry, which has been employed to study the adsorption thermodynamics of a number of isothiocyanato Cr(III) complexes that are electroreduced via ligand-bridged processes at mercury electrodes.[14] However, this technique suffers from the important limitation that for systems that require bulk adsorbate concentrations above ca. 1×10^{-3} M in order to induce significant surface concentrations ($>1 \times 10^{-11}$ mol cm^{-2}), the detection of this adsorption from the Faradaic charge–time intercept becomes very difficult. Therefore, values of K_{e} (surface adsorbate concentration/bulk concentration) below ca. 1×10^{-5} cm cannot easily be evaluated using this technique. However, detection methods based upon the effect of the adsorbate on the double-layer structure rather than the Faradaic charge consumed in its oxidation or reduction do not suffer from this limitation. One such method is based on the rate response of simple outer-sphere electrode reactions to the addition of the adsorbing species. We have recently found that the outer-sphere electroreductions of cobalt(III)–ammine complexes are sensitive and reliable reactions with which to monitor the specific adsorption of various anions at the mercury–aqueous interface.[10,25] Such "kinetic probes" should also provide a sensitive means of detecting the presence of more complex ionic adsorbates. Thus the addition of $Cr(NH_3)_5NCS^{2+}$, for example, produces significant decreases in the electroreduction rate of $Co(NH_3)_5F^{2+}$ at mercury electrodes, arising from the electrostatic repulsion between the cationic adsorbed complex and the cationic reactant. ($Co(NH_3)_5F^{2+}$ is reduced in the potential range −200 to −500 mV vs. SCE which is prior to the electroreduction of most Cr(III) complexes.[1]) The extent of this rate decrease is somewhat (ca. threefold) smaller than expected on the basis of the known adsorption of $Cr(NH_3)_5NCS^{2+}$ [14,26] coupled with the simple Gouy–Chapman–Stern–Frumkin model of double-layer effects in electrode kinetics, which has been found to describe successfully the effects of adsorbed anions.[10,25] (This result is not unexpected since adsorbed $Cr(NH_3)_5NCS^{2+}$ is unlikely to resemble a cationic point charge precisely.) Nevertheless, the method does provide a useful semiquantitative measure of the adsorption of a number of the complexes which are of interest here. Details of this application will be given elsewhere.[15] Of the chromium(III)– and cobalt(III)–azido and –isothiocyanato complexes of present interest, the specific adsorption of only $Cr(NH_3)_5NCS^{2+}$ can be successfully detected using chronocoulometry.[19,26] However, the specific adsorptions of $Cr(OH_2)_5NCS^{2+}$ and $Cr(NH_3)_5N_3^{2+}$ were detected from the significant drop in the $Co(NH_3)_5F^{2+}$ reduction rate which results from the addition of these complexes to a large excess of supporting electrolyte (KF or $NaClO_4$). The addition of $Cr(OH_2)_5N_3^{2+}$ produced no detectable rate change in the adsorbate concentration range studied ($\lesssim$10 mM). The extent of adsorption was quantified using a "calibration curve" of rate decrease vs. adsorbate concentration derived for the $Cr(NH_3)_5NCS^{2+}$ system. In each case, the surface adsorbate concentration Γ was sufficiently low that Henry's law should apply; i.e., Γ is proportional to the bulk adsorbate concentration at a given electrode potential,[14] and therefore K_{e} is independent of Γ.

The resulting estimates of K_{e} for $Cr(NH_3)_5NCS^{2+}$, $Cr(OH_2)_5NCS^{2+}$, and $Cr(NH_3)_5N_3^{2+}$ at mercury electrodes are given in Table I. Scrutiny of these data reveals that the values of K_{e} for free NCS^-, N_3^-, and the corresponding pentaammine- and pentaaquochromium(III) complexes do not differ greatly, especially at potentials close to the potential of zero charge (ca. −450 mV vs. SCE) where electrostatic diffuse-layer effects upon K_{e} will be least important. The potential dependence of K_{e} is markedly less for such complexes compared with that of the free anions, which is probably due to the electrostatic effect of the Cr(III) center. Nevertheless, as previously discussed,[14] the effect of the bridging anion predominates because its center of charge is located more deeply within the double-layer region. The significantly (but not substantially) stronger adsorption of ammine complexes vs. the corresponding aquo complexes has also been noted previously and ascribed to ligand field stabilization effects upon the ligand–metal surface bond.[26]

These values of K_{e} correspond to the stability constants for the precursor states K_{e}^{p} for the inner-sphere electroreduction of these complexes. The corresponding values of K_{e}^{s} (i.e., for

Table I. Adsorption Thermodynamics ($-\log K_e$ Values[a]) of Some $Cr^{III}X$ Complexes and Corresponding Free Anions X at the Mercury-Aqueous Interface at 25 °C

adsorbate	electrolyte	$-E$, mV vs. SCE 200	 300	 400	 500	 600	 700
NCS^- [b,e]	1 M KF			4.6	5.0	5.5	5.9
$Cr(NH_3)_5NCS^{2+}$ [c,f]	0.5 M $NaClO_4$, 0.32 M H_2SO_4	4.4	4.4	4.4	4.5	4.7	4.9
$Cr(OH_2)_5NCS^{2+}$ [d]	0.5 M $NaClO_4$	~4.8		~4.9			
N_3^- [b,g]	0.1 M NaN_3			~5.5	~6.0	~6.5	
$Cr(NH_3)_5N_3^{2+}$ [d]	1 M KF		5.8	6.0			
$Cr(OH_2)_5N_3^{2+}$ [d]	0.5 M $NaClO_4$		>6.0				
Br^- [b,h]	1 M KF	4.0	4.5	5.0	5.6	6.1	
$Cr(NH_3)_5Br^{2+}$ [d]	0.5 M $NaClO_4$		5.0	~5.2			
Cl^- [b,i]	1 M KF	5.4	5.9	6.45	6.95	7.45	
$Cr(NH_3)_5Cl^{2+}$ [d]	0.5 M $NaClO_4$		5.4	~5.7			
$Cr(OH_2)_5Cl^{2+}$ [d]	0.5 M $NaClO_4$		>6.0				

[a] K_e is the adsorption coefficient (stability constant) of the adsorbate which equals surface concentration/bulk concentration (cm). Measurement conditions are known (or assumed) to approximate Henry's law for the adsorbate. [b] Determined from electrode capacitance measurements. [c] Determined using chronocoulometry. [d] Determined using the kinetic probe method (see text). [e] Reference 9. [f] Reference 18 and 26. [g] C. V. D'Alkaine, E. R. Gonzalez, and R. Parsons, *J. Electroanal. Chem.*, **32,** 57 (1971). [h] A. R. Sears and P. A. Lyons, *J. Electroanal. Chem.*, **42,** 69 (1973). [i] R. Payne, *Trans. Faraday Soc.*, **64,** 1638 (1968).

Table II. Rate Constants and Relative Reorganization Energies of Inner- and Outer-Sphere Pathways for the Electroreduction of Some Chromium(III) and Cobalt(III) Complexes at the Mercury-Aqueous Interface

complex	$-E$, mV vs. SCE	outer-sphere pathways k_e^E, cm s^{-1}	 K_e^p,[i] cm	 $(\Delta G_e^{\ddagger\text{-p}})^E$,[k] kcal mol^{-1}	inner-sphere pathways k_e^E, cm s^{-1}	 K_e^p,[j] cm	 $(\Delta G_e^{\ddagger\text{-p}})^E$,[k] kcal mol^{-1}
$Cr(NH_3)_5N_3^{2+}$	600	6×10^{-7} [a,d,g]	3×10^{-7}	17.4	$\sim 5 \times 10^{-7}$ [a,d,g]	5×10^{-7}	17.8
$Cr(OH_2)_5N_3^{2+}$	600				2×10^{-5} [b,e]	$\sim 2 \times 10^{-7}$	15.0
$Cr(NH_3)_5NCS^{2+}$	600				1×10^{-5} [a,d]	2×10^{-5}	18.0
$Cr(OH_2)_5NCS^{2+}$	600				7×10^{-4} [b,e]	5×10^{-6}	14.8
$Co(NH_3)_5NCS^{2+}$	200	$\sim 1 \times 10^{-3}$ [c,f,h]	9×10^{-9}	10.8	~0.3[c,f,g]	4×10^{-5}	12.4
$Co(NH_3)_5N_3^{2+}$	200	$\sim 4 \times 10^{-3}$ [c,f,g] $\sim 2 \times 10^{-3}$ [c,f,h]	9×10^{-9}	10.0 10.4	$\sim 1 \times 10^{-2}$ [c,f,g]	2×10^{-6}	12.6
$Cr(NH_3)_5Cl^{2+}$	600	3×10^{-6} [a,d,g]	3×10^{-7}	16.4	1×10^{-5} [a,d,g]	$\sim 1 \times 10^{-6}$	16.4
$Cr(NH_3)_5Br^{2+}$	600				6×10^{-3} [a,e]	$\sim 3 \times 10^{-6}$	13.2

[a] Data from ref 1. [b] Data from ref 8. [c] Data from ref 10. [d] Determined in 40 mM $LaCl_3$ or $La(ClO_4)_3$. [e] Determined in 1 M $NaClO_4$. [f] Determined in 1 M KF. [g] Estimated from extent of rate increases resulting from addition of adsorbing I^- or Br^- at constant ionic strength compared with those for analogous yet pure outer-sphere pathways (see text and ref 1). [h] Estimated assuming that difference in outer-sphere rates between a series of complexes is the same for both homogeneous and electrochemical reduction using a fixed reductant and electrode potential, respectively[2] (see ref 10 for relevant rate data). [i] Determined from $K_e^p = 2r \exp(-ZF\phi_r/RT)$. r is effective radius of reactant (taken as 3×10^{-8} cm) and Z is net charge on ion. ϕ_r is electrostatic potential at the reaction site with respect to bulk solution[1,10] which was estimated from Gouy-Chapman-Stern theory using electrode charge-potential data gathered in the appropriate electrolyte (M. J. Weaver and F. C. Anson, *J. Electroanal. Chem.*, **65,** 711 (1975)). [j] Taken or extrapolated from data in Table I (K_e^p for Co(III) complexes assumed to be the same as for corresponding Cr(III) complex). [k] From listed values of k_e^E and K_e^p using eq 1a and assuming that $\nu_e^p = 10^{13}$ s^{-1}.

the corresponding Cr(II) complexes) cannot be obtained experimentally due to the substitutional lability of Cr(II). However, since the degree of interaction between Cr(II) and the bridging ligand will be smaller than for Cr(III), it is very likely that K_e^s also closely mirrors K_e for the free anions NCS^- and N_3^-.

Extraction of absolute estimates of $(\Delta G_e^{\ddagger})^i$ from the experimental rate data additionally requires knowledge of the standard potentials $E°$. Unfortunately, these are not known with any certainty for the majority of the systems of interest here. However, *relative* values of $(\Delta G_e^{\ddagger})^i$ for corresponding inner- and inter-sphere mechanisms can still be obtained from eq 1 if the electroreduction rates of these two processes are known along with the work terms $RT \ln K_e^p$ and $RT \ln K_e^s$. Three reactions involving azide and isothiocyanato complexes provide suitable systems: the electroreduction of $Cr(NH_3)_5N_3^{2+}$, $Co(NH_3)_5N_3^{2+}$, and $Co(NH_3)_5NCS^{2+}$. The first two reactants appear to be reduced via mixed mechanisms where both inner- and outer-sphere pathways contribute significantly to the measured rates.[1,10] Thus rate enhancements were found upon the addition of specifically adsorbing anions but were significantly smaller and had a different dependence upon the electrode potential than analogous pure outer-sphere reductions.[1,10] As the incidence of pure anion-bridged pathways is signaled by small rate *decreases* under these conditions rather than the large rate enhancements seen for outer-sphere pathways, the rate observed in the presence of moderate anionic specific adsorption in the case where significant rate enhancements were observed should correspond approximately to that for the outer-sphere pathway. The outer-sphere rate corresponding to the absence of anionic specific adsorption was then obtained by applying the double-layer correction known to apply to similar yet pure outer-sphere pathways.[1] Although $Co(NH_3)_5NCS^{2+}$ reduces via an essentially pure inner-sphere pathway, the rate for the corresponding outer-sphere pathway can be estimated to a useful approximation by the use of homogeneous-heterogeneous rate correlations.[10] For the reduction of $Co(NH_3)_5N_3^{2+}$, where both these methods could be employed, the resulting outer-sphere rates are in reasonable agreement (Table II).

The resulting rate constants referring to these pathways are listed in Table II, along with the corresponding estimates of $(\Delta G_e^{\ddagger\text{-p}})^E$. (The electrode potentials $E = -600$ and -200 mV were chosen for the Cr(III) and Co(III) reduction reactions, respectively, so as to facilitate an intercomparison of the ligand effects while minimizing the extent of extrapolation of rate-potential data that was required.) These latter quantities were obtained by inserting the rate constants into eq 1a along with the required estimates of K_e^p, assuming that $\nu^p \approx 10^{13}$ s^{-1}. For outer-sphere reactions, K_e^p was estimated using the relation $K_e^p = 2r \exp(-ZF\phi_r/RT)$, where r is the effective radius of the reactant (taken to be 3×10^{-8} cm), Z is its net charge, and ϕ_r is the electrostatic potential at the reaction site with respect to the bulk solution.[1,10] (The term $2r$ essentially converts the *three*-dimensional reactant concentration within the vicinity of the reaction site into an effective *two*-dimensional concentration on the reaction plane.) For inner-sphere reactions, the appropriate values of K_e^p at the chosen electrode potential E were taken (or extrapolated) from the data in Table I. (The values of K_e^p for $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5N_3^{2+}$ were assumed to be the same as for the corresponding Cr(III) complexes.) Since it is expected that $K_e^p \approx K_e^s$ for these systems, then the relative values of $(\Delta G_e^{\ddagger-p})^E$ for each system should closely mirror the required relative values of $(\Delta G_e^{\ddagger})^i$ (see eq 1b).

Inspection of Table II reveals that $(\Delta G_e^{\ddagger-p})^E$ for the three inner-sphere pathways is similar or marginally larger than for the corresponding outer-sphere pathways: there is no evidence that this reorganization energy is significantly lowered by ligand bridging. This result also supports the assumption that the outer-sphere pathways are adiabatic, because otherwise the large increase in the transmission coefficient[2] expected for the ligand-bridged pathway would yield an apparent lowering of $\Delta G_e^{\ddagger-p}$. It therefore appears that the role of the isothiocyanate or azide bridging ligand is simply to alter the stability of the transition state by an amount approximately equal to the ground-state energy of bond formation between these ligands and the mercury surface. The reorganization of the Cr(III) or Co(III) centers and the surrounding solvent that is required prior to electron transfer does not appear to be aided by their attachment via these ligands to the electrode surface. This result is perhaps not surprising since the length of these polyatomic ligands will place the Cr(III) and Co(III) centers about 6 Å from the electrode surface, which is similar to the value estimated for the reaction planes for the corresponding outer-sphere pathways.[1,10] The flexibility of these ligands should allow similar vibrational interactions with the surrounding water molecules in both cases.

This conclusion probably also applies to the azido and isothiocyanato systems in Table II for which the electroreduction rates and hence $\Delta G_e^{\ddagger-p}$ for the outer-sphere pathways are not known. Thus $\Delta G_e^{\ddagger-p}$ for the inner-sphere electroreduction of corresponding $Co(NH_3)_5X^{2+}$, $Cr(NH_3)_5X^{2+}$, and $Cr(OH_2)_5X^{2+}$ complexes are all closely similar, and NCS^- and N_3^- have comparable coordinating properties.[28] It therefore appears that these bridges act to catalyze electrochemical Cr(III)/Cr(II) and Co(III)/Co(II) redox reactions at the mercury–aqueous interface merely by altering the "preexponential factor" associated with the work terms $RT \ln K_e^p$ and $RT \ln K_e^s$ and do not significantly lower the intrinsic barrier to electron transfer $(\Delta G_e^{\ddagger})^i$.

Other Ligand Bridges. It might be expected that smaller ligands such as the halide anions would be more effective than azide or thiocyanate in catalyzing electrochemical reactions by lowering $\Delta G_e^{\ddagger-p}$ and $(\Delta G_e^{\ddagger})^i$. The reacting metal center would then be located closer to the electrode surface where strong orbital overlap with the electrode surface atoms[13,21] and a smaller contribution from solvent repolarization[2,3] could significantly lower the reorganization energy. Indeed, the inner-sphere electroreduction rates of some chloro– and bromo–chromium(III) complexes are substantially larger than for other complexes of similar structure.[1,8] However, thermodynamic (driving force) factors are undoubtedly responsible for at least part of these rate differences.[8]

The specific adsorptions of $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Br^{2+}$ (but not $Cr(OH_2)_5Cl^{2+}$) were detected using the kinetic probe method: the resulting estimates of K_e^p are given in Table I along with K_e for free chloride and bromide anions. These values of K_e^p for $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Br^{2+}$ are markedly closer than for the corresponding free anions. Of these complexes, $Cr(NH_3)_5Cl^{2+}$ is apparently reduced with both inner- and outer-sphere pathways contributing significantly to the observed rates.[1] The rate constants, together with the resulting pair of estimates of $\Delta G_e^{\ddagger-p}$, are given in Table II. Again the resulting values of $\Delta G_e^{\ddagger-p}$ are found to be very similar. However, the relationship of $\Delta G_e^{\ddagger-p}$ to $(\Delta G_e^{\ddagger})^i$ is more tenuous for this system because K_e^s and K_e^p could well be significantly different. Nevertheless, the intrinsic barriers for the inner- and outer-sphere electroreduction pathways for $Cr(NH_3)_5Cl^{2+}$ are unlikely to differ by more than ca. 1 kcal mol^{-1} based on the observed differences between K_e^p and K_e for free chloride ions (Table I).

At least part of the decrease in $(\Delta G_e^{\ddagger-p})^E$ for inner-sphere reactions in the sequence $Cr(NH_3)_5NCS^{2+}$, $Cr(NH_3)_5N_3^{2+} > Cr(NH_3)_5Cl^{2+} > Cr(NH_3)_5Br^{2+}$ (Table II) can be ascribed to the variation of the driving force term $0.5F(E - E°)$ for the redox couples $Cr(NH_3)_5X^{2+} + e^- \rightleftarrows Cr(NH_3)_5X^+$. Although the required values of $E°$ are unknown, the variation in $E°$ can be roughly estimated from the relative stability constants for CrX^{2+} complexes.[29,31] Thus, from the known stability constants K_X^{III} for $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5NCS^{2+}$,[32] an approximate (at least upper limit) difference in $0.5F(E - E°)$ between these systems of ca. 1.3 kcal mol^{-1} is obtained, which indeed corresponds closely to the difference in $\Delta G_e^{\ddagger-p}$ for the inner-sphere reduction of these complexes (Table II). Although K_X^{III} is unknown for $Cr(NH_3)_5Br^{2+}$, inspection of the corresponding stability data for $Cr(OH_2)_5X^{2+}$ complexes[33] again reveals that a lower value of $\Delta G_e^{\ddagger-p}$ for $Cr(NH_3)_5Br^{2+}$ relative to $Cr(NH_3)_5Cl^{2+}$ is expected, as observed. However, small yet significant variations in $(\Delta G_e^{\ddagger-p})^i$ would well account for part of these differences in $\Delta G_e^{\ddagger-p}$ as the bridging ligand is varied.

Comparison with Corresponding Homogeneous Ligand-Bridged Processes. Of particular interest is the comparison of the effects of a given series of bridging ligands in catalyzing corresponding electrochemical and chemical electron-transfer reactions. For outer-sphere reactions, the theoretical prediction that $(\Delta G_e^{\ddagger})^i \approx 0.5(\Delta G_c^{\ddagger})^i$ for the corresponding exchange reactions[2,3] is on the whole consistent with the measured rates of a number of electrochemical and chemical processes.[2b,4,5] These and other rate correlations are based on the assertion that the intrinsic barriers are simple additive properties of the particular reactants involved.[2] It has been suggested that these relationships which were derived for weakly adiabatic processes may also be valid for some inner-sphere reactions;[21] in fact, some success has been achieved in the application of the Marcus "cross-reaction" correlation[2b] to a few homogeneous inner-sphere reactions.[11a]

Consider the inner-sphere electrochemical and chemical reactions of eq 3 and 4, where M_1 and M_2 represent metal ions

$$M^{III}{}_1X + e^-(E) \rightarrow M^{II}{}_1X \tag{3a}$$

$$M^{II}{}_2X - e^-(E) \rightarrow M^{III}{}_2X \tag{3b}$$

$$M^{III}{}_1X + M^{II}{}_2 \rightarrow M^{II}{}_1 + M^{III}{}_2X \tag{4}$$

and X is a bridging ligand. The close physical relationship between these reactions can be seen by comparing the "precursor complex" for the combination of (3a) and (3b), $M^{III}{}_1X\text{–MS–}XM^{II}{}_2$, with the precursor complex for reaction 4, $M^{III}{}_1X\text{–}M^{II}{}_2$ (MS denotes metal electrode surface). It is expected that little or no rearrangement of the ligand–electrode bonds are required during heterogeneous electron transfer. The close analogy between outer-sphere heterogeneous and homogeneous processes[2b] is therefore maintained for ligand-bridged pathways, although a single bridging ligand is common to both reactants only in the latter processes. If both reacting centers $M^{III}{}_1$ and $M^{II}{}_2$ are activated in an identical manner in both reactions 3 and 4, then it follows that the intrinsic

Table III. Estimated Intrinsic Barriers for Homogeneous and Heterogeneous $Cr^{III}(OH_2)_5X/Cr^{II}(OH_2)_5X$ Electron-Exchange Reactions

	homogeneous exchange				heterogeneous exchange			
oxidant	k_c,[a] $M^{-1}\ s^{-1}$	pathway[b]	$(\Delta G_c^{\ddagger})^i$,[c] kcal mol^{-1}	$-E_X°$,[d] mV vs. SCE	$10^5 k_e^{EX}$,[e] cm s^{-1}	pathway[b]	K_e^p,[f] cm	$(\Delta G_e^{\ddagger})^i$,[g] kcal mol^{-1}
$Cr(OH_2)_6^{3+}$	$\sim 10^{-9}$ [h]	o.s.	~29	655	0.75[l]	o.s.	2×10^{-8}	14.2
$Cr(OH_2)_5F^{2+}$	2×10^{-2} [i]	i.s.	<22.5	860	0.6[l]	o.s.	1.5×10^{-8}	14.2
$Cr(OH_2)_5N_3^{2+}$	6[j]	i.s.	<19.2	~725	12[l]	i.s.	$\sim 5 \times 10^{-8}$	~13
$Cr(OH_2)_5NCS^{2+}$				725	420[l]	i.s.	$\sim 1 \times 10^{-6}$	~12.8
$Cr(OH_2)_5Cl^{2+}$	~30[k]	i.s.	<18.3	590	120[l]	i.s.	$\sim 5 \times 10^{-8}$	~12

[a] Second-order rate constant for homogeneous reduction by Cr^{2+}; acid-independent pathway. Rates measured at (or extrapolated to) 25 °C and $\mu = 1$. [b] i.s. denotes inner-sphere pathway; o.s. denotes outer-sphere pathway. [c] Intrinsic barrier for homogeneous self-exchange reaction, estimated from k_c using eq 2 in text. Required values of K_c^p ($=K_c^s$ for self-exchange reactions) are estimated as follows. For outer-sphere $Cr(OH_2)_6^{3+/2+}$ exchange, calculated as $\sim 0.2\ M^{-1}$ from eq 34 of ref 13 using $r = 6 \times 10^{-8}$ cm, ionic strength $\mu = 1$ M. For inner-sphere reactions, K_c is taken as $<100\ M^{-1}$ (see text). ν^p is taken as $10\ s^{-1}$.[13] [d] Estimated standard potential for couple $Cr^{III}X + e^- \rightleftarrows Cr^{II}X$.[29] See ref 8 for details and data sources. [e] Heterogeneous rate constant for $Cr^{III}X/Cr^{II}X$ couple at mercury–aqueous interface measured at $E_X°$. [f] Precursor complex formation constant for appropriate electrochemical reduction pathway. For outer-sphere reactions, estimated from $K_e^p = 2r \exp(-ZF\phi_r/RT)$ (see text). For inner-sphere reactions, K_e^p is assumed to equal that for the corresponding free anion (Table I; see text). [g] Intrinsic barrier for heterogeneous exchange reaction at mercury–aqueous interface, estimated from $k_e^{EX°}$ and K_e^p using eq 1. ν^p was taken as $10^{13}\ s^{-1}$.[13] [h] See ref 35. [i] D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958). [j] R. Snellgrove and E. L. King, *Inorg. Chem.*, 3, 288 (1964). [k] R. V. James and E. L. King, *ibid.*, 9, 1301 (1970). [l] Reference 8.

barrier $(\Delta G_c^{\ddagger})_{12}^i$ for the homogeneous reaction (4) should again equal the sum of the intrinsic barriers $(\Delta G_e^{\ddagger})_1^i$ and $(\Delta G_e^{\ddagger})_2^i$ for the electrochemical reactions 3a and 3b.

The simplest comparison of this type is for self-exchange reactions, i.e., where $M_1 = M_2$, so that $(\Delta G_e^{\ddagger})_1^i = (\Delta G_e^{\ddagger})_2^i$. Rate constants for some corresponding chemical and electrochemical Cr(III)/Cr(II) exchange reactions that are mediated by bridging ligands and for outer-sphere $Cr(OH_2)_6^{3+/2+}$ exchange are listed in Table III. The latter homogeneous self-exchange rate is not directly measurable due to a dominant acid-dependent pathway in the rate law.[34] The value listed was obtained from application of the Marcus "cross-relation"[2b] using experimental rate data for outer-sphere reductions by Cr^{2+}.[35] The electrochemical rate constants are those measured at the formal potential, $E_x°$, for the appropriate $Cr^{III}X/Cr^{II}X$ couple where the overall driving force $(E - E_x°)$ will be zero as for the homogeneous self-exchange reactions. Approximate estimates of $E_x°$ can be obtained for these systems.[8,29] Inspection of these rate parameters reveals that much greater exchange rate enhancements result from the insertion of a bridging ligand into the Cr^{III} and Cr^{II} coordination shells for homogeneous compared to the corresponding heterogeneous processes. To estimate $(\Delta G_c^{\ddagger})^i$ and $(\Delta G_e^{\ddagger})^i$ from k_c and $k_e^{Ex°}$ using eq 1 and 2, estimates of K^p and K^s are required; $\Delta G_c°$ and $(E - E°)$ are both equal to zero. The values of K_c^p (which equal K_c^s for these self-exchange reactions) are unknown. However, upper limits for $(\Delta G_c^{\ddagger})^i$ can be estimated with confidence by noting that K_c^p is very unlikely to exceed 100 M^{-1}, because higher values should yield large deviations from the observed second-order rate laws.[42] (In all probability, the true values of K_c^p are much smaller, as are the chromous-anion stability constants.[8]) Nevertheless, the resulting upper limits for $(\Delta G_c^{\ddagger})^i$ are substantially smaller than $(\Delta G_c^{\ddagger})^i$ for outer-sphere $Cr(OH_2)_6^{3+/2+}$ exchange (Table III).

In order to estimate the corresponding values of $(\Delta G_c^{\ddagger})^i$, values of K_e^p and K_e^s are required. In lieu of experimental values, rough estimates were obtained by using the values for the corresponding free anions at $E_X°$ (Table I). The data in Table I indicate that this assumption is not likely to produce more than a 1–2 kcal mol^{-1} error in $(\Delta G_e^{\ddagger})^i$. Although the resulting estimates of $(\Delta G_e^{\ddagger})^i$ in Table III can therefore be considered to be very approximate, the substantial lowering of $(\Delta G_c^{\ddagger})^i$ by the simple bridging anions is not seen for $(\Delta G_e^{\ddagger})^i$ (Table III). Thus for the outer-sphere $Cr(OH_2)_6^{3+/2+}$ exchange, $(\Delta G_e^{\ddagger})^i \approx 0.5(\Delta G_c^{\ddagger})^i$ as predicted by the Marcus model,[2b] but for the inner-sphere Cr(III)/Cr(II) reactions, $(\Delta G_e^{\ddagger})^i > 0.5(\Delta G_c^{\ddagger})^i$. This conclusion is also applicable to the reductions of the corresponding $Cr(NH_3)_5X^{2+}$ complexes. Thus these complexes are electroreduced via inner-sphere mechanisms at a fixed electrode potential about a hundredfold slower than the corresponding $Cr(OH_2)_5X^{2+}$ complexes.[1] This is approximately the same rate ratio as observed for their homogeneous inner-sphere reduction by Cr^{2+},[1] which is expected if the intrinsic barriers are increased by the same amount for the homogeneous and heterogeneous processes and the work terms remain unaltered.

It seems likely that this behavioral difference arises from a decrease in the intrinsic barrier for the homogeneous inner-sphere exchange reactions due to strong mutual interactions ("communication") between the Cr(III) and Cr(II) reacting centers. Such effects can arise by means of electronic coupling between the two reacting centers, leading to a splitting of the potential energy curves in the intersection region.[12,13,43] Such coupling is expected to occur especially when electron transfer occurs between reactant and product orbitals of the same symmetry.[44] Alternatively, the presence of a ligand common to both redox centers may lower the overall reorganization energy by a complementary motion of the ligand toward Cr(II) and away from Cr(III), thus helping to achieve the necessary bond distortion at both redox centers which is required in order for electron transfer to occur.[45] The very great preference of Cr^{2+} for homogeneous inner- rather than outer-sphere pathways is also seen in the reduction of cobalt(III)–ammine complexes, where the electron is also transferred between e_g orbitals.[45] Significantly smaller rate enhancements resulting from inner-sphere pathways are seen when the electron is transferred between orbitals of different symmetries.[45]

It therefore is not too surprising that no significant decreases in $\Delta G_e^{\ddagger-p}$ occur for the present electrochemical systems in going from an outer-sphere to an inner-sphere pathway. Thus no strong chemical interactions are expected between the bridging ligands with the mercury surface, and only one redox center is required to be activated in order for electron transfer to occur. If such a circumstance is commonly the case, then the incidence of electrochemical ligand-bridged reaction pathways may be substantially less widespread than in homogeneous redox chemistry. Additionally, the catalysis arising from heterogeneous inner-sphere pathways will be limited by the number of available surface sites for strongly adsorbed intermediates. However, with more "catalytically active" electrode surfaces, such as platinum, the markedly larger reactant–electrode interactions that are expected[46] could yield substantial reductions in the size of the intrinsic barrier for such inner-sphere pathways. Some preliminary data for the electroreduction of pentaammine–cobalt(III) complexes at platinum and gold electrodes support this notion. Thus the inner-sphere electroreduction of $Co(NH_3)_5Cl^{2+}$ at the platinum–aqueous interface has been found to be favored over the corresponding outer-sphere pathway by ca. 10^5,[47] which is too large an effect to be easily ascribed to changes in the thermodynamic (work term) factors. Further experiments aimed at unraveling the roles of bridging ligands in catalyzing electrochemical reactions at solid electrode surfaces are currently in progress in our laboratory.

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Registry No. $Cr(NH_3)_5NCS^{2+}$, 16884-60-9; $Cr(OH_2)_5NCS^{2+}$, 22258-89-5; $Cr(NH_3)_5N_3^{2+}$, 22317-10-8; $Cr(OH_2)_5N_3^{2+}$, 18517-09-4; $Cr(NH_3)_5Br^{2+}$, 22289-65-2; $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $Cr(OH_2)_5Cl^{2+}$, 14404-08-1; $Cr(OH_2)_6^{3+}$, 14873-01-9; $Cr(OH_2)_5F^{2+}$, 19559-07-0; $Co(NH_3)_5NCS^{2+}$, 14970-18-4; $Co(NH_3)_5N_3^{2+}$, 14403-83-9.

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(35) The Marcus "cross-relation"[2b] between homogeneous self-exchange and cross-reactions is $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$. For the reduction of a common oxidant, 1, by reductants 2 and 3 and by assuming that $f_{12} \approx f_{13}$ we can write $k_{12}/k_{13} = (k_{22}K_{23}/k_{33})^{1/2}$. For a number of outer-sphere reductions by Cr^{2+} and V^{2+}, $k_{V^{II}}/k_{Cr^{II}} = k_{12}/k_{13} \approx 50$.[36] As $K_{23} = 2.5 \times 10^3$ [37] and k_{22} ($V^{3+/2+}$ exchange) = 1×10^{-2} M^{-1} s^{-1},[38] then k_{33} ($Cr^{3+/2+}$ exchange) = 1.5×10^{-9} M^{-1} s^{-1}. Also, for a few outer-sphere reductions by Cr^{2+} and $Ru(NH_3)_6^{2+}$, $k_{Ru^{II}}/k_{Cr^{II}} = k_{12}/k_{13} \approx 500$.[39] As $K_{23} = 1 \times 10^8$ [40] and k_{22} ($Ru(NH_3)_6^{3+/2+}$ exchange) = 8×10^2 M^{-1} s^{-1},[41] then k_{33} ($Cr^{3+/2+}$ exchange) $\approx 10^{-10}$ M^{-1} s^{-1}.
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(39) Reference 11a, p 326.
(40) Calculated from formal potentials for $Cr^{3+/2+}$ (−655 mV vs. SCE[30]) and $Ru(NH_3)_6^{3+/2+}$ (−190 mV vs. SCE for $\mu \approx 0.1$, given in H. S. Lin, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972)).
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